

# High Energy Density Ultracapacitors

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*This presentation does not contain any proprietary or confidential information.*

# Overview

## Timeline

- Project Start Date: 2008
- Project End Date: 2012
- 20% Complete

## Barriers

- Energy Density
- Affordability
- Shelf Life/Self Discharge

## Budget

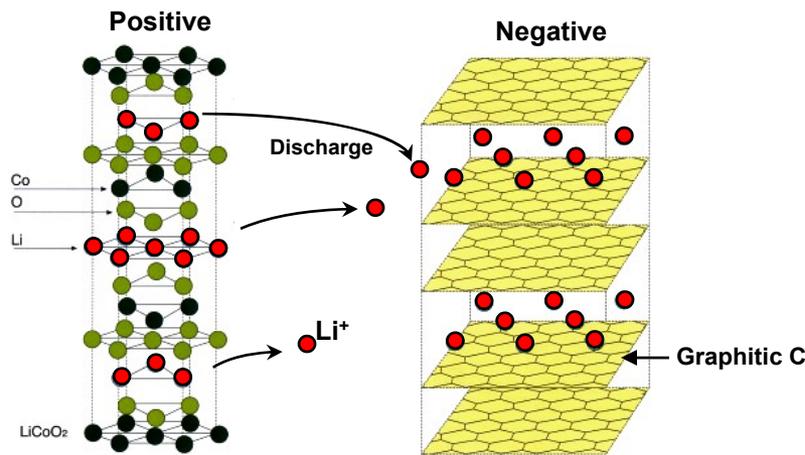
- Funding received in FY08: \$200K
- Funding for FY09: \$250K
- Project cost shared by Navy

## Collaborators

- Glenn Amatucci, Rutgers University
- Deyang Qu, University of Massachusetts, Boston
- Robert Waterhouse, Entek Membranes

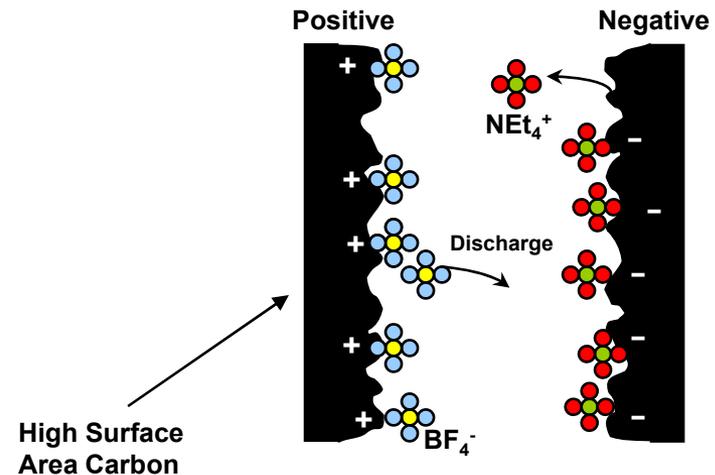
Background

- Lithium ion batteries known for their high energy densities (~200 Wh/kg) can be engineered to deliver high power (1000 W/kg). The number of times they can be recharged, however, is usually less than 1000 cycles.
- Electrochemical double layer capacitors (also referred to as supercapacitors or ultracapacitors) store energy within the electrochemical double layer occurring at the electrode/electrolyte interface. They are known for their high power capability and exceptional cycle life (>>100,000 cycles) but low energy densities (3-5 Wh/kg). These cells are referred to as Symmetrical Capacitors because they utilize two identical carbon electrodes.



### Lithium Ion Battery

Contains two, Faradaic electrode materials



### Electrochemical Double Layer Capacitor

Contains two, non-Faradaic electrode materials

- To increase the energy density of electrochemical double layer capacitors (EDLCs) while maintaining their high power capability and long cycle life, efforts are now focusing on developing new energy storage devices referred to as Asymmetric Capacitors. These devices couple electrodes that undergo Faradaic reactions (e.g. battery materials) with those that display capacitive behavior (high surface area carbons). Asymmetric capacitors have a higher energy density than their symmetric counterpart due to increased capacitance and higher cell operating voltages ( $E = \frac{1}{2}CV^2$ ).

### Symmetric Double Layer Capacitor

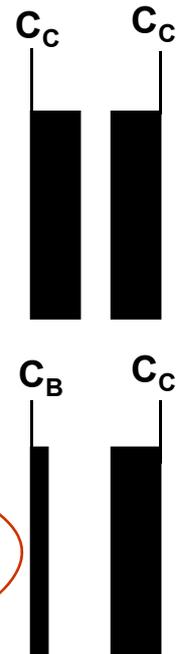
- Comprised of two highly-porous Carbon Electrodes ( $C_C$ ) of equal capacitance
- Overall device capacitance equal to  $\frac{1}{2}C_C$ :

$$\frac{1}{C} = \frac{1}{C_C} + \frac{1}{C_C} \quad \text{yields} \quad C = \frac{C_C}{2}$$

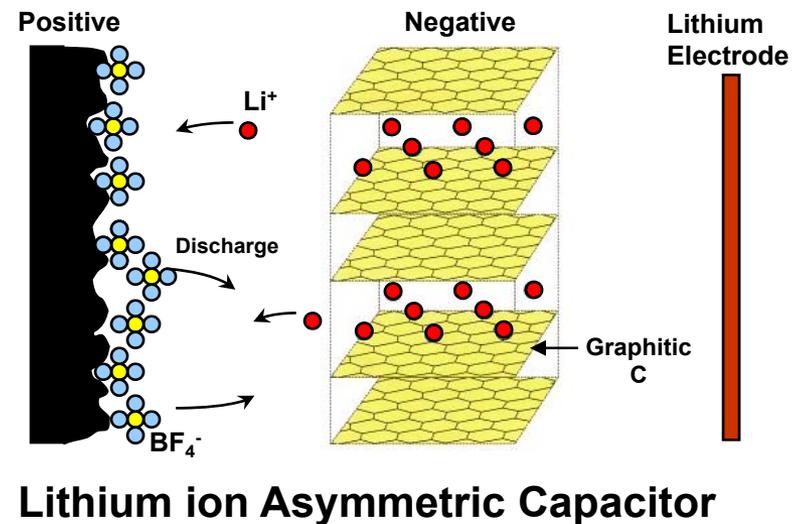
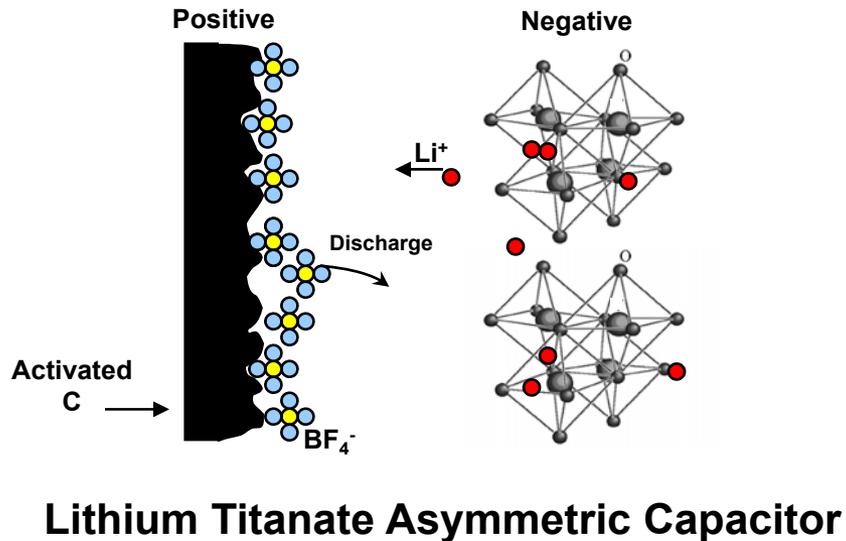
### Asymmetric Double Layer Capacitor

- Battery Electrode ( $C_B$ ) provides a much greater capacitance than Capacitor Electrode ( $C_C$ ) in much less volume
- Overall device capacitance equal to  $C_C$ :

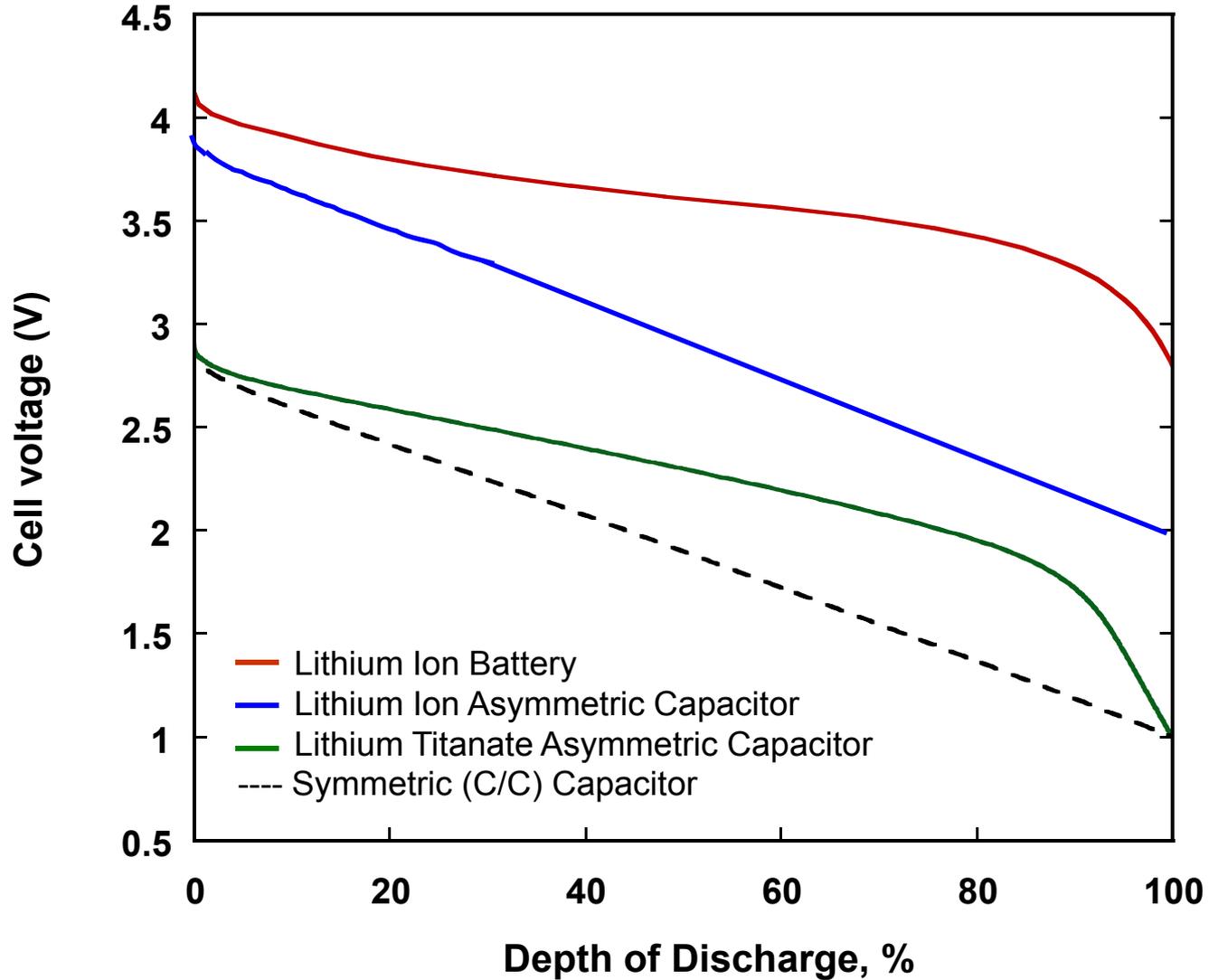
$$\frac{1}{C} = \frac{1}{C_C} + \frac{1}{C_B} \quad \text{where } C_B \gg C_C \quad \text{yields} \quad C = C_C$$



- One class of asymmetric capacitors utilizes a negative battery electrode that intercalates lithium ions. Nanostructured lithium titanate ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) asymmetric capacitors have demonstrated outstanding cycle life (1 million cycles - G. Amatucci). This unusually high recharge capability is due to the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  spinel structure. It exhibits  $< 1\%$  volume change during the ionic intercalation. Another system, referred to as lithium ion capacitors, utilizes a graphitic carbon ( $\text{Li}_x\text{C}_6$ ) that must be pre-doped with lithium prior to use. The  $\text{Li}_x\text{C}_6$  capacitor demonstrates high voltage capability (3.8V).
- The energy density of both of these systems, however, is limited by the activated carbon's low capacity.

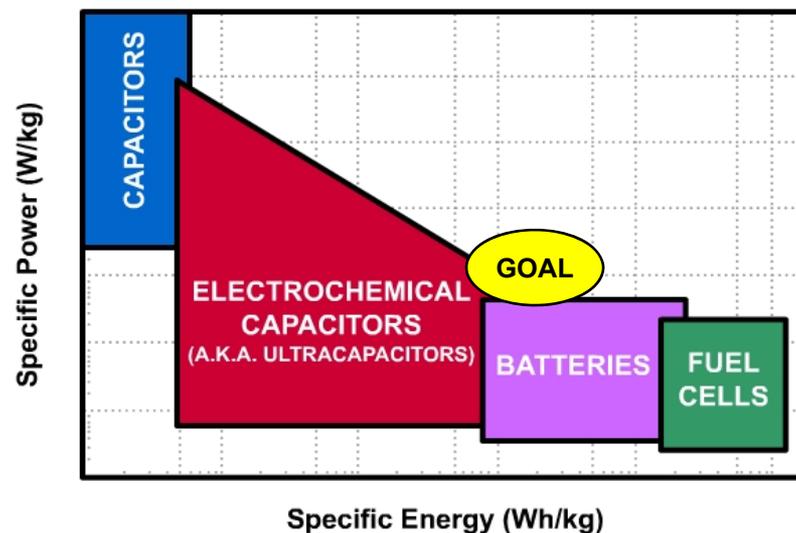


# Comparison of Voltage Profiles



# Objectives

- Identify high capacity (capacitance) carbon materials to increase the energy density of Asymmetric Capacitors utilizing a lithium ion-type negative electrode. Understand the physicochemical properties responsible for high capacity.
- Develop electrolyte solvent systems that have a wide electrochemical voltage window and will allow the cell to operate between  $-30$  to  $+50$  °C and survive between  $-45$  to  $+65$  °C.
- Design, fabricate and evaluate prototype capacitors, in order to assess the advantages/disadvantages of the lithium titanate and graphitic carbon systems in terms of energy density, cycle life, self-discharge and safety.

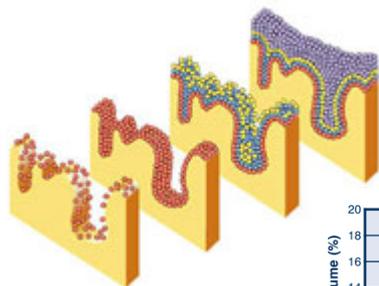


# Milestones

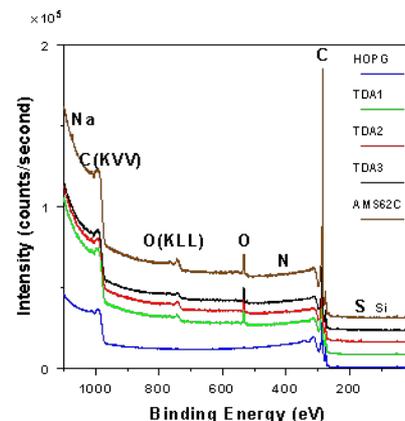
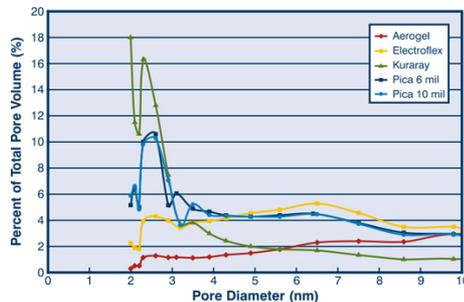
Task	FY08				FY09				FY10				FY11				FY12			
	1Q	2Q	3Q	4Q																
Carbon surface area/pore size analysis	█				█				█											
Symmetric (C/C) pouch cell evaluation	█				█				█											
Electrode processing evaluation	█				█				█											
Carbon functional group analysis					█				█				█							
1/2 cell positive electrode evaluation					█				█				█							
Electrolyte stability investigation					█				█				█							
Shelf life investigation					█				█				█							
1/2 Cell negative electrode evaluation					█				█				█							
3-Electrode laboratory cell evaluation									█				█				█			
Asymmetric pouch cell evaluation													█				█			

# Approach

- Activated carbons will be obtained from various carbon suppliers including small businesses and universities. Their physicochemical properties will be characterized using such techniques as Brunauer-Emmett-Teller Surface Area (to determine surface area and average pore-size distribution) and X-Ray Photoelectron/Fourier Transform Infrared/Raman Spectroscopy (to determine the amount of residual oxygen, nitrogen, and sulfur containing groups).
- Various electrode processing techniques will be assessed to ensure that the benefits of high capacitance carbons aren't diminished with pore-blocking binders.
- Pouch (2" by 3") and 3-electrode laboratory cells will be fabricated for electrochemical evaluation via galvanostatic cycling, cyclic voltammetry and AC Impedance.
- Various electrolyte solvent mixtures will be studied systematically to elucidate the influence of such properties as conductivity and voltage stability window on cell capacitance and self-discharge.
- Self-discharge will be defined using small, electrochemical research cells containing reference electrodes. The causes of self discharge will be identified by comparing the degree of voltage drop with the carbon's functional groups and impurities.



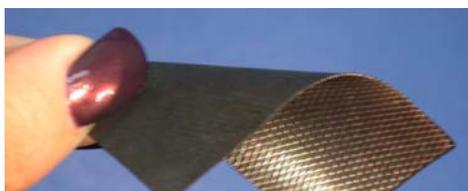
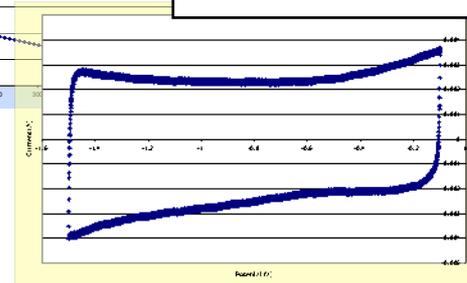
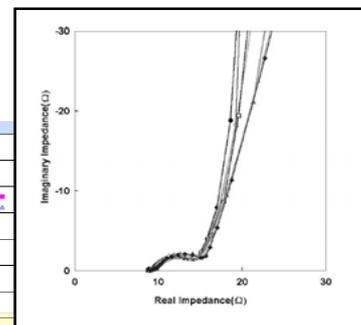
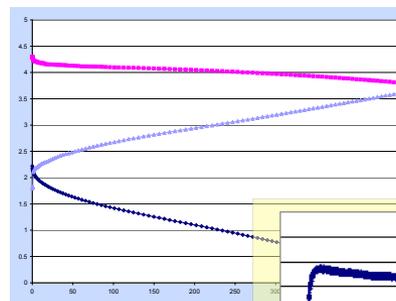
## Commercial and Developmental Carbons



## Physical & Chemical Analysis



2" x 3" Pouch Cells

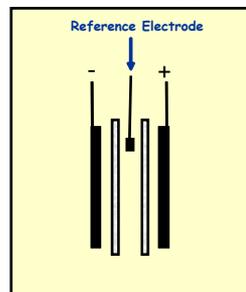


Electrode Fabrication



Lab Cell

3-Electrode Cell



## Electrochemical Analysis

# Accomplishments To Date

# Physical Characteristics of Carbon Powders

Carbon	Supplier	Precursor	Activation Process	Country	BET Surface Area (m <sup>2</sup> /g)	Av. Pore Size (nm)
Grade 1 Cloth	MarkeTech International	Resorcinol Formaldehyde	None	USA	402	4.14
RP-15	Kuraray	Phenolic Resin	Steam	Japan	1318	1.94
YP-17D	Kuraray	Coconut Shell	Steam	Japan	1516	2.03
YP-18X	Kuraray	Coconut Shell	Steam	Japan	1479	2.38
NK-260	Kuraray	Mesophase Pitch	KOH	Japan	2040	1.92
NK-261	Kuraray	Mesophase Pitch	KOH	Japan	2300*	TBD
NK-331	Kuraray	Mesophase Pitch	KOH	Japan	1100*	TBD
Nuchar RGC	MeadWestvaco	Mixed Hardwood	Chemical	USA	1622	2.99
Supra 50	Norit	Coconut Shell	Steam	Netherlands	1989	2.05
SX-Ultra	Norit	Peat	Steam	Netherlands	969	3.49
BP-10	Pica	Pine Saw Dust	Steam	France	1796	2.95
TDA-1	TDA	Sucrose	CO <sub>2</sub>	USA	2053	2.04
TDA-2	TDA	Sucrose	CO <sub>2</sub>	USA	2114	1.90
TDA-3	TDA	Fructose, Glucose	CO <sub>2</sub>	USA	2265	2.35
TDA-AMS 62C	TDA	Fructose, Glucose	CO <sub>2</sub>	USA	1939	1.99
Generation 1	U of Kentucky	Filtration Carbon	Steam	USA	1907*	2.46*
Generation 2	U of Kentucky	Filtration Carbon	CO <sub>2</sub>	USA	1783*	2.06*
YEC-07	Fuzhou Yihuan	Unknown	Unknown	China	2600*	TBD

\* Provided by supplier.

- Eighteen carbon powders have been investigated to date. Powder surface areas ranged from 402 to 2,600 m<sup>2</sup>/g. The average pore size range from 1.90 to 4.14 nm.

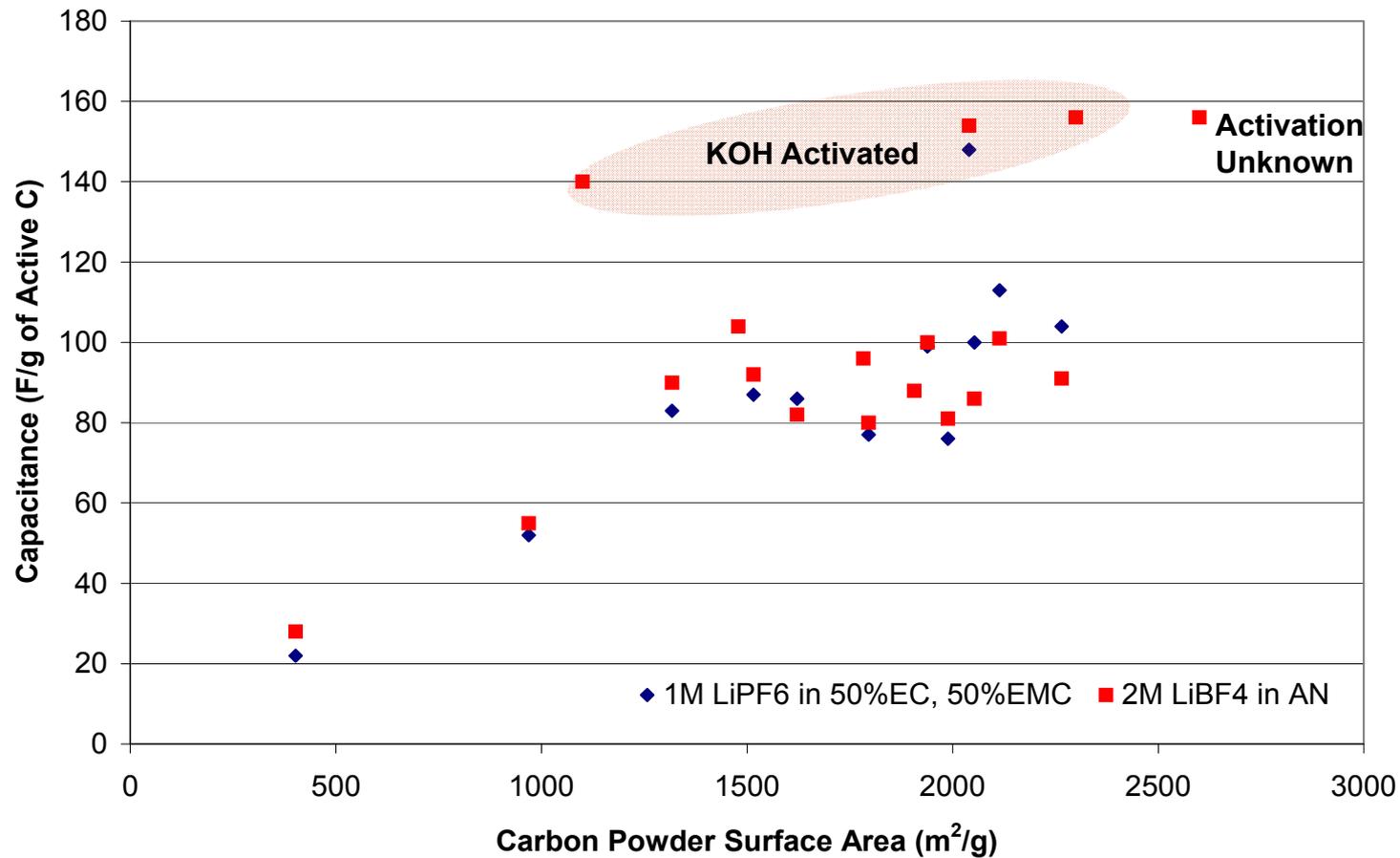
# Capacitance of Various Carbon Cells

2" X 3" Symmetric Cells, Cells Charged at 1mA/cm<sup>2</sup> and Discharged at 10mA/cm<sup>2</sup>, Capacitance of 50<sup>th</sup> discharge

<b>Carbon</b> (% active Material)	<b>Carbon Supplier</b>	<b>Binder</b>	<b>1M LiPF<sub>6</sub></b> <b>50%EC:50%EMC</b> <b>(F/g)</b>	<b>2M LiBF<sub>4</sub></b> <b>AN</b> <b>(F/g)</b>
Grade 1 (100)	MarkeTech International	none	22	28
RP-15 (92)	Kuraray	UHMWPE	83	90
YP-18X (84)	Kuraray	UHMWPE	87	92
YP-17D (82)	Kuraray	UHMWPE	TBD	104
NK-260 (80)	Kuraray	UHMWPE	148	154
NK-261 (82)	Kuraray	UHMWPE	TBD	156
NK-331 (80)	Kuraray	UHMWPE	TBD	140
Nuchar RGC (80)	MeadWestvaco	UHMWPE	86	82
Supra 50 (80)	Norit	UHMWPE	76	81
SX-Ultra (80)	Norit	UHMWPE	52	55
BP-10 (80)	Pica	UHMWPE	77	80
TDA-1 (81)	TDA	PVDF	100	86
TDA-2 (81)	TDA	PVDF	113	101
TDA-3 (81)	TDA	PVDF	104	91
TDA-AMS 62C (81)	TDA	PVDF	99	100
Generation 1 (80)	U of Kentucky	PVDF	TBD	88
Generation 2 (82)	U of Kentucky	UHMWPE	TBD	96
YEC-07 (82)	Fuzhou Yihuan	UHMWPE	TBD	156

- Carbons were formed into electrodes using a low cost manufacturing process developed by ENTEK Membranes (ElectroFlex®) when sufficient quantities of carbon were available. This process is based on the continuous extrusion and extraction of porous films filled with activated carbon, and is made possible by gel-processing of ultrahigh molecular weight polyethylene (UHMWPE). The amount of binder and conductive carbon was typically 10 weight percent each. When carbon quantities were limited, electrodes were made using a doctor-blade process and contained 9 weight percent polyvinylidene fluoride (PVDF) and 10 weight percent conductive carbon.
- Galvanostatic cycling of symmetric pouch cells revealed that the highest capacitance was achieved with cells containing Kuraray NK-261 and Fuzhou Yihuan YEC-07 (156F/g). Cells utilizing  $\text{LiBF}_4$  in acetonitrile generally displayed higher capacitance than those containing  $\text{LiPF}_6$  in 50% ethylene carbonate: 50% ethyl methyl carbonate. This correlates with their conductivity, 17.3 mS/cm and 9.5 mS/cm, respectively. Several carbon powders made from carbohydrate sugars, however, demonstrated higher capacitance in lithium-based carbonate electrolytes.

# Effect of Carbon Powder Surface Area on Cell Capacitance

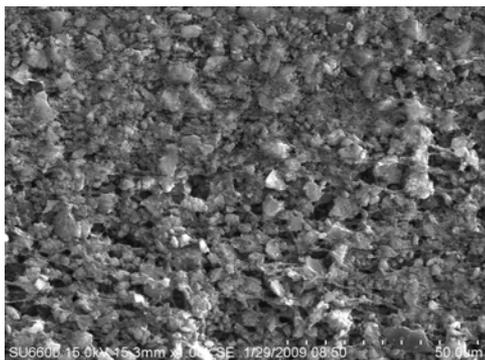
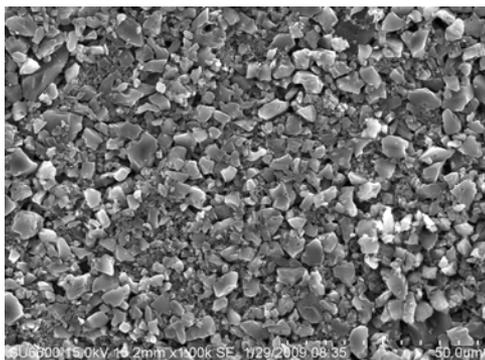
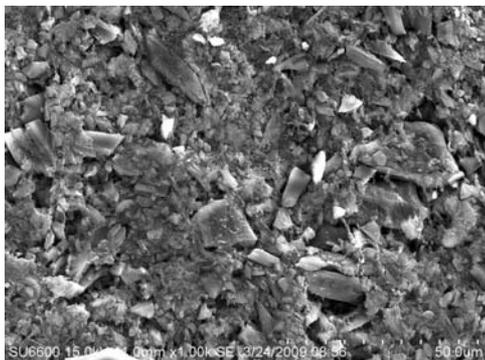


- The general dependence of the cell's capacitance on the carbon powder's surface area is observed in the data above. The aerogel cloth, having the lowest surface area (402 m<sup>2</sup>/g), displayed the lowest capacitance of the carbons investigated, while carbons having the high surface areas displayed the highest capacitance.

# Evaluation of Electrode Processing

(Using Kuraray YP-17D Carbon)

## SEM of Electrodes



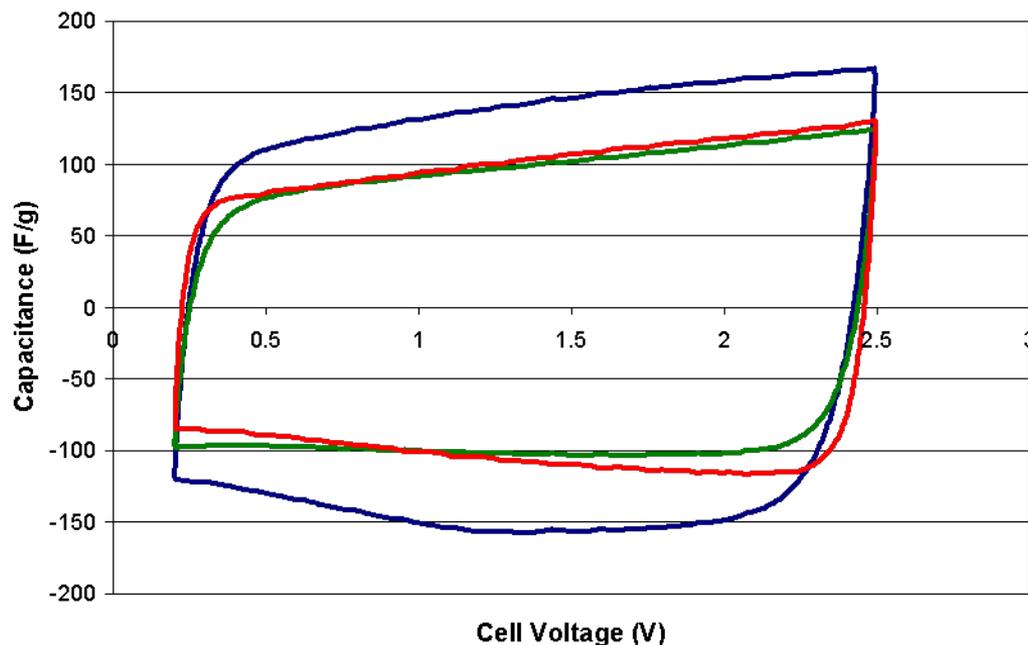
A

B

C

1000x  
magnification

2" x 3" electrode cells, 20 mV/s, 2M LiBF<sub>4</sub> in acetonitrile,  
50<sup>th</sup> cycle



■ Commercial Process A: 134 F/g

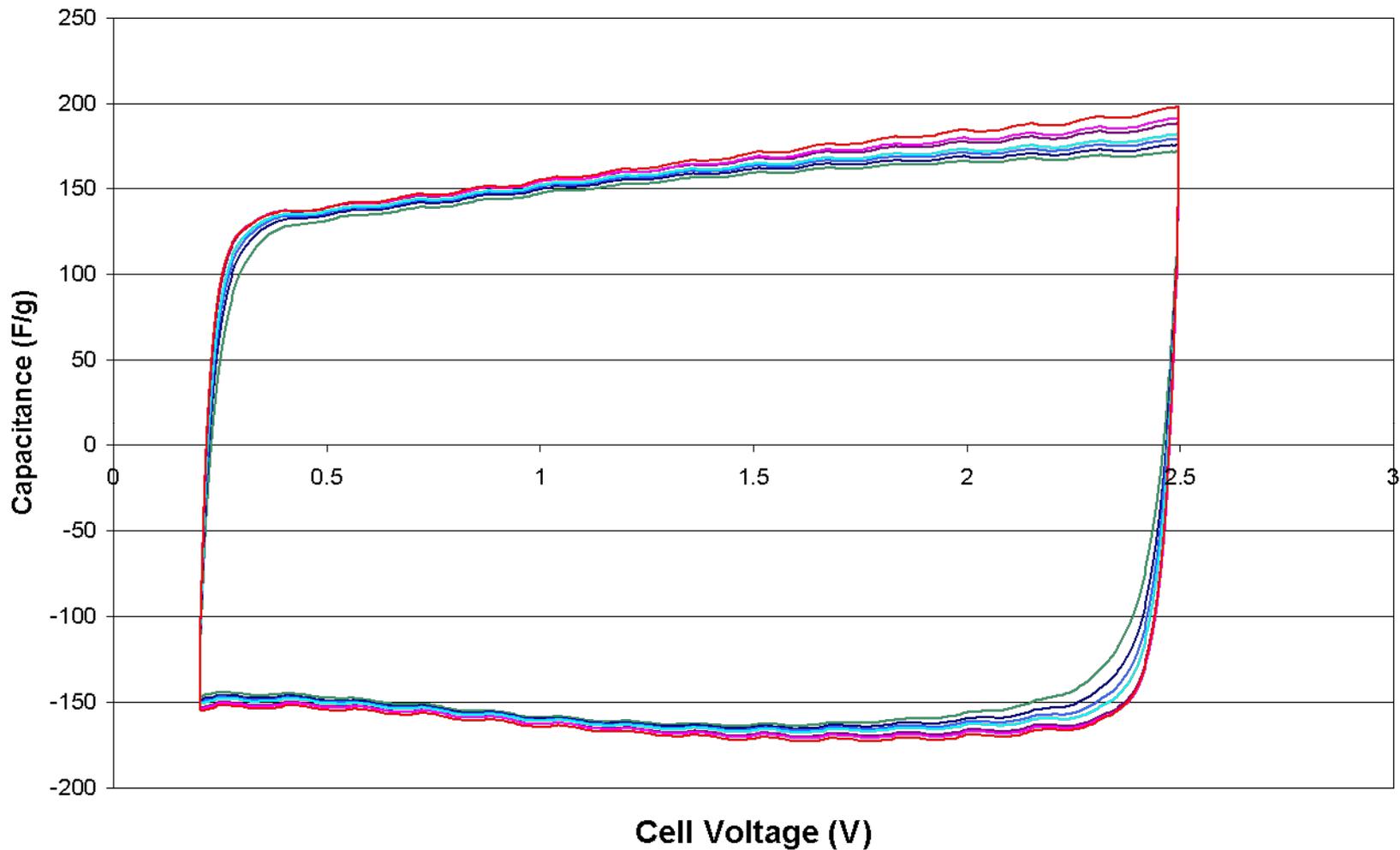
■ NSWC Process B: 94 F/g

■ Commercial Process C: 104 F/g

- Activated carbon is excellent electrode material for electrochemical double layer capacitors because of its high active surface area. However, activated carbon is not easily converted into useful electrodes. A high-performance electrode must maintain the carbon's high surface area as well as have good mechanical strength.
- Three electrode processes were examined:
  - Commercial Process A is proprietary and utilizes polytetrafluoroethylene as a binder. The electrode has exceptional mechanical integrity and gave the highest capacitance.
  - NSWC Process B utilizes a doctor-blade procedure where polyvinylidene fluoride is used as a binder. This process produced electrodes that were fragile and should only be used when limited sample quantities are available.
  - Commercial process C is based on the continuous extrusion and extraction of porous films filled with activated carbon and is made possible by gel-processing of ultrahigh molecular weight polyethylene. This process is expected to yield the most affordable electrodes of the processes examined. The electrodes have excellent mechanical integrity.

# Effect of Temperature on Cell Capacitance

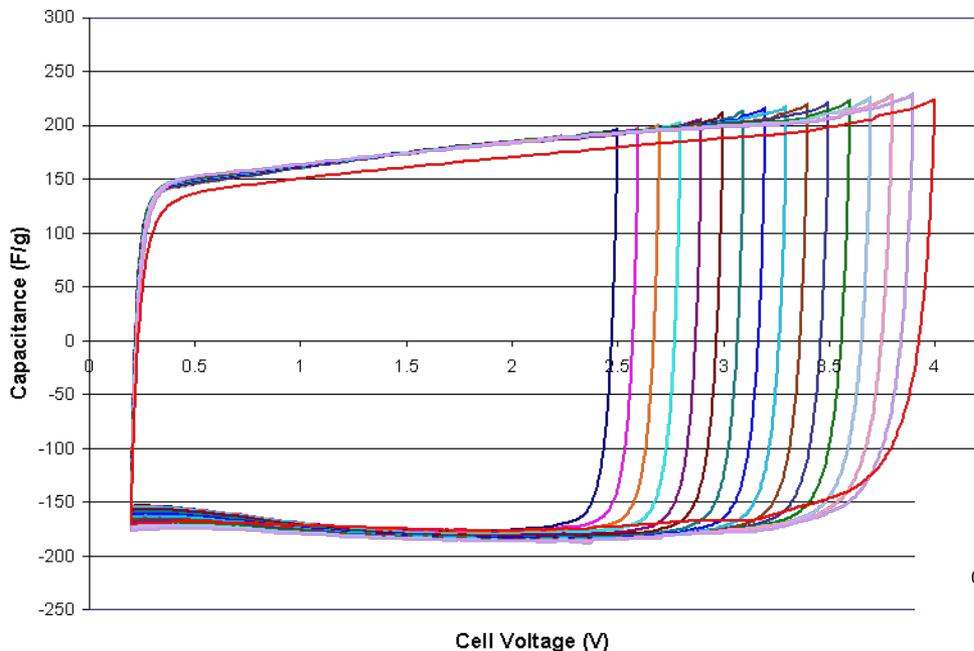
Kuraray NK261, 2M LiBF<sub>4</sub>, in Acetonitrile, 20mv/s



— -30°C — -20°C — -10°C — 0°C — 25°C — 40°C — 50°C

- The amount of energy that a capacitor delivers is governed by the potential difference between the two electrodes [ $E = 1/2C(\Delta V)^2$ ]. Organic electrolyte systems such as 2M LiBF<sub>4</sub> in acetonitrile have a wider tolerance in both the potential window and the operating temperature range than aqueous electrolytes.
- The acetonitrile electrolyte displayed excellent performance between -30 and +50°C. The capacitance value varied less than 5% over this temperature range.

# Effect of Voltage Limits on Cycling Efficiency



Kuraray NK261

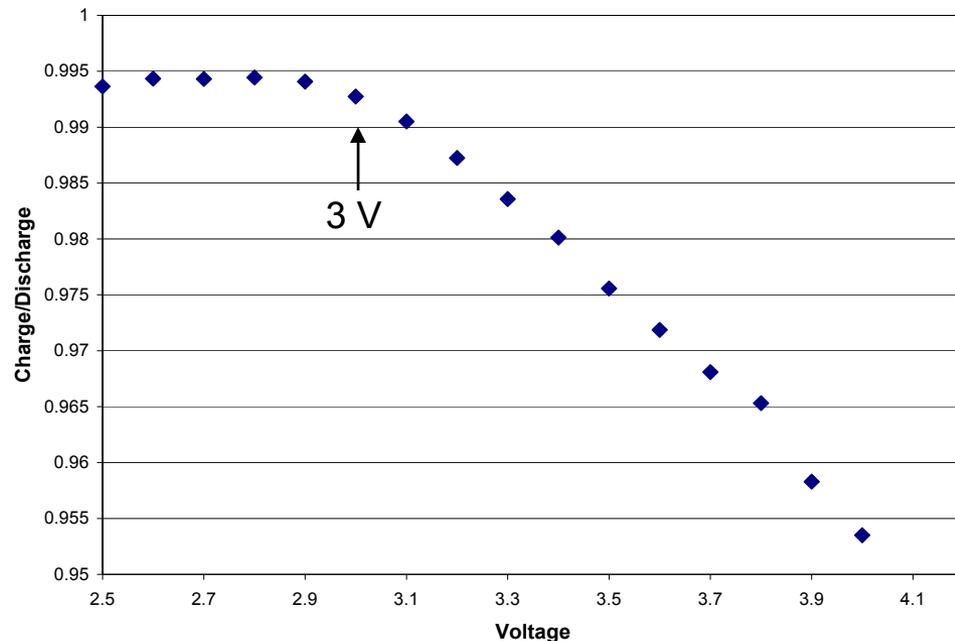
2M LiBF<sub>4</sub> in Acetonitrile

25°C

Cells were cycled 50 times prior to this experiment (0.2 to 2.5V)

- Potential window of electrolyte examined using cyclic voltammetry.
- Ideally a cycling efficiency = 1 indicates the absence of irreversible redox reactions.
- The acetonitrile electrolyte appears to decomposed on the Kuraray NK261 electrode at approximately 3V.

$$\text{Cycling Efficiency} = Q_{\text{Discharge}} / Q_{\text{Charge}}$$



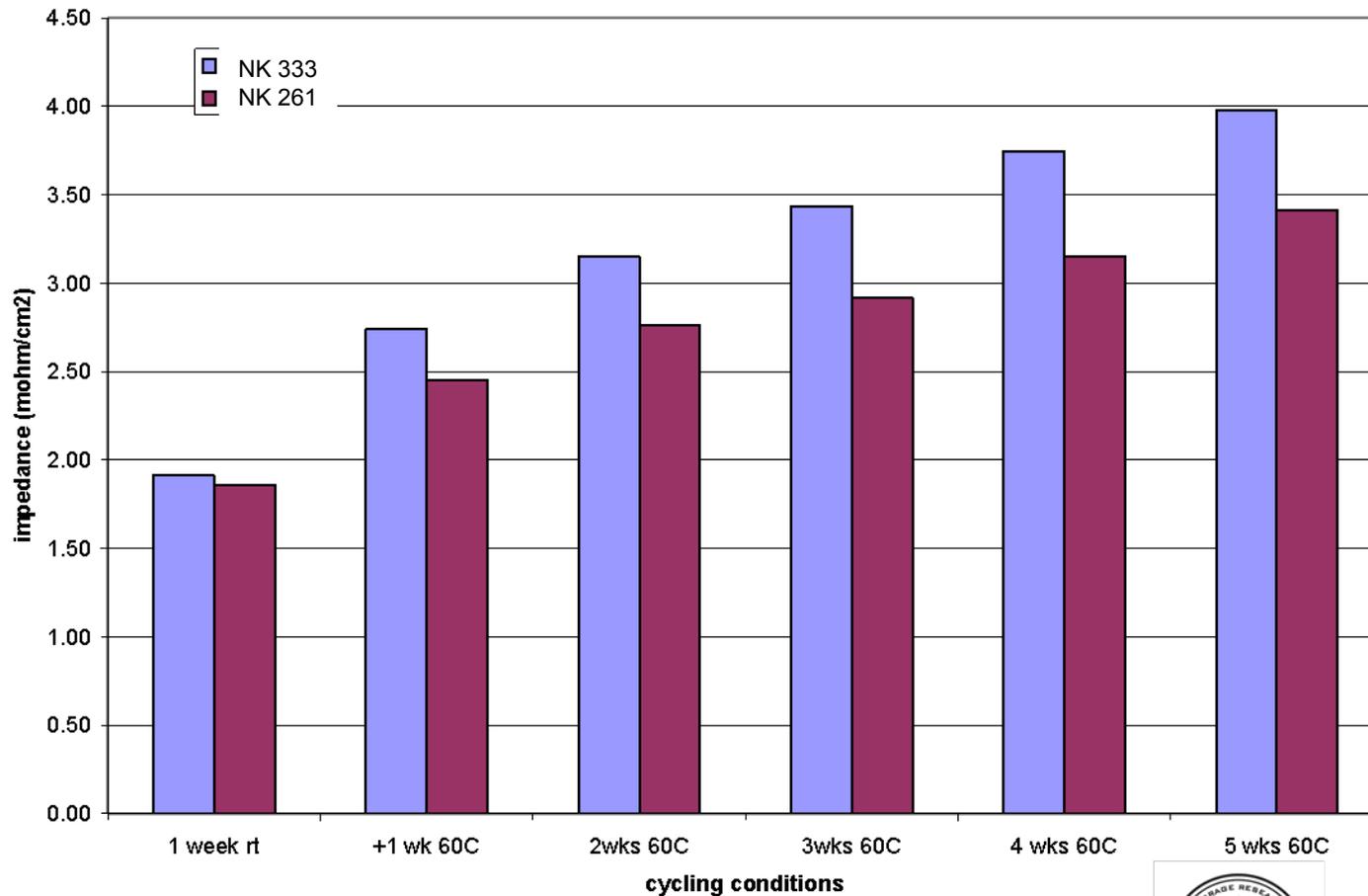
- The potential window of the electrolyte was investigated using cyclic voltammetry. Prior to this experiment, the cell was cycled 50 times (0.2 – 2.5V).
- The peaks on the top right of the cyclic voltammograms indicate the occurrence of irreversible redox reactions. The cycling efficiency was calculated using the formula,

$$\text{Cycling Efficiency (CF)} = (Q_{\text{Discharge}}/Q_{\text{Charge}})$$

- Ideally, CF = 1 indicates the absence of irreversible redox reactions. This cell showed a decline in cycling efficiency at approximately 3V.

# Impedance of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ Cells Using Different Carbons

Impedance 2M  $\text{LiBF}_4$  in AN, 2.5V constant storage, 60°C



- Glenn Amatucci (Rutgers University) fabricated  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$  cells containing Kuraray NK261 and Kuraray NK331. These carbons were found to be easily processed into electrodes and the resulting electrodes delivered good capacitance.
- Cells (2" by 3") were fabricated and cycled (1.5 to 2.7V) at various rates (C/2 to 50C), then charged to 2.5V and held at this voltage at 60°C for one week intervals. AC impedance of the discharged cell was measured every week at room temperature (22°C).
- These results indicate the importance of carbon type on cell stability when cells are subjected to high temperature, float-charge. The difference in cell performance may be the result of functional groups (oxygen, hydrogen) residing on the edges of graphitic particles. The groups may react with the electrolyte solvent at specific voltages and temperatures.

# Results

- The capacitance of eighteen carbons was determined using symmetric C/C pouch cells (2" by 3") containing organic electrolytes.
- KOH activated carbons displayed higher capacitance than those activated by steam or CO<sub>2</sub>.
- Cell capacitance was greater for cells containing 2M LiBF<sub>4</sub> in acetonitrile electrolyte than those containing 1M LiPF<sub>6</sub> in a mixture of ethylene carbonate and ethyl methyl carbonate (EC/EMC). One class of carbons, made from sugars, displayed the highest capacitance with 1M LiPF<sub>6</sub> EC/EMC.
- The general dependence of the cell's capacitance on carbon powder's surface area was observed.
- Electrode processing was found to be important.
- Prototype lithium titanate asymmetric capacitors revealed the importance of carbon type on shelf life, especially if cells are stored in the charged state at high temperatures.

# Future Work

## FY09

- Efforts will continue to identify high capacitance carbon materials utilizing symmetric 2-electrode pouch cells. Capacitance will be correlated to the carbon's physicochemical properties.
- The most promising carbons will be investigated using 3-electrode laboratory cells containing references to follow individual electrode performance. 3-Electrode performance data will be compared to the 2-electrode pouch cells.

## FY10

- High capacitance carbons will be coupled to lithium ion and lithium titanate negative electrodes in hermetically-sealed, 2" by 3" pouch asymmetric capacitor cells. These cells will undergo a series of electrochemical experiments (cyclic voltammetry, galvanostatic cycling, AC impedance) to evaluate the benefits and limitations of the two systems. Cells will be evaluated in terms of energy density and cycle life. Information obtained will be used to down-select the negative electrode material ( $\text{Li}_x\text{C}_6$  or  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) for further investigation.
- The shelf discharge behavior of asymmetric capacitors will be investigated utilizing 3-electrode laboratory cells. The information obtained will be correlated to carbon's functional groups.

# Summary

## **Objective:**

- Investigations are underway to develop lithium ion ( $\text{Li}_x\text{C}_6$  or  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) asymmetric electrochemical capacitors. Their high capacitance values and operating voltages promise significantly higher energy densities ( $\geq 12$  Wh/kg) than symmetric C/C capacitors (3-5 Wh/kg).

## **Approach:**

- In order to realize the full promise of these new energy storage devices, higher capacitance carbons and electrolytes that are stable over a wide over a wide potential window will be identified [ $E = 1/2C(\Delta V)^2$ ].

## **Accomplishments:**

- The electrochemical performance of numerous carbon materials were investigated and correlated to their surface area and pore size utilizing 2' by 3" pouch cells. Excellent performance ( $\sim 160$  F/g) was observed with carbons activated using potassium hydroxide (KOH).

## **Future Work:**

- High capacitance carbons will be coupled to lithium titanate and lithium ion electrodes to assess the asymmetric cells' energy density and cycle life.
- Shelf discharge behavior will be investigated utilizing 3-electrode laboratory cells and correlated to carbon's functional groups.